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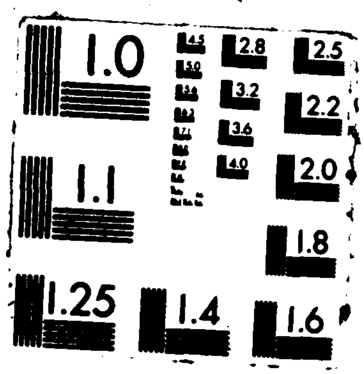
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TECHNICAL REPORT ARCCD-TR-87003

AD-A181 365

ELIMINATION OF AIRBORNE LEAD CONTAMINATION FROM CALIBER.22 AMMUNITION

RAYMOND BRANDS

JUNE 1987

US ARMY
ARMAMENT
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Many indoor firing ranges have been ordered closed due to high levels of toxic airborne lead contamination. The source of much of this contamination is the caliber .22 rimfire ammunition used for marksmanship training. This program proved the feasibility of a non-toxic caliber .22 rimfire cartridge.

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INTRODUCTION

Indoor firing ranges are used by military and civilian organizations for firearms training. These ranges offer year round marksmanship training regardless of climate or geographical situations. The problem of high concentrations of toxic lead contamination in many ranges has resulted in their closure until ventilation improvements are made or ammunition is developed which does not contaminate the ranges. The U.S. Training and Doctrine Command tasked the U.S. Army Armament, Research, Development and Engineering Center (ARDEC) to determine if the sources of lead contamination could be eliminated from caliber .22 ammunition. The program evaluated the feasibility of eliminating lead contamination from caliber .22 ammunition since it is the most common ammunition fired in military indoor ranges. The development of low cost, non-contaminating caliber .22 ammunition would eliminate health hazards introduced by airborne lead and would provide for the continuation of indoor marksmanship training without the need to install and maintain additional expensive air ventilation/filtration systems.

BACKGROUND

The Occupational Safety and Health Act of 1970 (OSHA) established standards for exposure to various toxic substances including airborne lead which is produced when small arms ammunition is fired. When the atmosphere inside firing ranges was tested, many ranges were found to exceed the OSHA established level of 0.5 milligrams per cubic meter of air. This airborne contamination was determined to be the primary cause of range workers' health problems in that over time the toxic heavy metals accumulated in their bodies. Personnel inhaled the airborne contamination and ingested the contaminates which settled on food or beverages. The four principle sources of airborne lead contamination from caliber .22 ammunition are:

- The cartridge primer mixture
- The lead projectile base to burning propellant interface
- The lead projectile to weapon bore interface
- The lead projectile to bullet trap interface

To reduce the airborne lead contamination hazard, temporary measures were implemented which included improving the range ventilation systems and reducing personnel exposure time. Additionally, ammunition manufacturers began to address the contamination problem through development of centerfire training ammunition with non-toxic metal or plastic bullet jackets completely inclosing the lead bullet core. The jacketed ammunition, however, did not fully eliminate the contamination because approximately 30% of the primer composition is comprised of the toxic heavy metals: lead and barium. The barium, however, is considered a minor contributor to the contamination problem due to its relatively small quantity and toxicity level. The ammunition manufacturers have not introduced non-contaminating caliber .22 rimfire ammunition due to the difficulties involved with producing a reliable lead-free primer mixture and the cost increase which may be incurred in changing the projectile's material.

The caliber .22 ammunition is used in rimfire rifles, rimfire pistols, and in centerfire M16 rifles. The prototype ammunition was required to cycle the M16 centerfire rifle with a special conversion bolt and magazine to permit the use of rimfire ammunition. The Army adopted the conversion kit for the M16 rifle since the use of rimfire ammunition meets many of the training scenarios while providing substantial cost savings over the use of centerfire ammunition.

In January 1984, a description of the work necessary to determine the feasibility of a non-contaminating rimfire cartridge was developed. Companies interested in conducting ammunition research were invited to submit proposals for evaluation. Based on the proposal evaluations, contract DAAK10-85-C-0034 was awarded to Olin Corporation, Winchester Group to conduct the feasibility study. The description of work required by Olin Corporation is the following:

- Evaluate alternatives to the current, all lead projectile, including plastics, composite materials, and sintered metals, as well as other concepts which would eliminate the contamination caused by the projectile base, weapon bore, and the bullet trap

- Evaluate non-contaminating primers and propellants and match the combination of primers and propellants to the candidate projectiles

- Conduct an engineering analysis and tests of the materials, manufacturing processes, component design, primer and propellant selection which best accomplish the objective of eliminating airborne lead contamination. Emphasis was to be on safety, functioning, reliability, primer snesitivity, accuracy, estimated production costs, and the prevention of other airborne contamination

- The results and the rational for the selection of a prototype configuration were to be conveyed to the government for approval. Two thousand prototype cartridges were to be produced for final testing at this facility once government approval was granted. Five hundred prototype cartridges were to be produced and shipped to ARDEC for a government evaluation of the contamination produced by the ammunition

The testing to be conducted by the contractor and government consisted of a matrix of chamber pressure, accuracy, velocity in test barrels, M16 rifles, and commercial rifles. See table 1 for the tests to be performed.

PROCEDURE

Upon award of the contract, Olin Corporation researched projectile designs and primer mixtures which would eliminate lead contamination without introducing other contamination sources. The decision was made not to investigate plastic or metal coating the current lead projectile to eliminate the possible source of lead contamination at the bullet trap. A solid plastic projectile concept was eliminated since a mathematical model indicated it would not produce the impulse required to cycle the M16 rifle. The model indicated that projectiles made of copper or an iron-polymer matrix were possible solutions. The copper alloy chosen for the projectile was tellurium copper, a copper alloy with 0.5% tellurium. Tellurium copper is frequently used for products requiring extensive machining and corrosion resistance.

The iron-polymer matrixes used in the experiment consited of 90% or more iron powder mixed with 10% or less of the polymers nylon and teflon. The mixtures were inserted into a projectile mold and heat fused to form the projectiles. Mixtures were also molded which contained an epoxy to bond the iron-polymer matrix without heat. The best iron-polymer matrix produced consisted of 94.5% powdered iron, with an average particle size of 40 microns, 5% nylon and 0.5% teflon. The contractor tested the iron-polymer projectile in standard production shellcases with the lead styphnate priming mixture and 2.9 grains of Winchester (WC371) propellant. This propellant quantity resulted in near the maximum recommended chamber pressure. The average velocity for the 21 grain projectile was 1404 feet per second. During testing, however, this projectile would not cycle the M16 rifle due to insufficient impulse energy. The powdered-iron projectiles were also brittle, resulting in two out of ten projectiles fracturing when fired in the test weapon. The impulse of the iron-polymer projectiles could not be increased enough to cycle the M16 rifle without exceeding the maximum pressure requirements; therefore, the iron-polymer design was eliminated.

A mathematical analysis of possible copper projectile designs indicated that a projectile in the 32 to 36 grain range was feasible with a 32 grain projectile being the best ballistic candidate (figure 1). Copper projectiles, weighing 32 grains, were screw machined with the same external dimensions as the 40 grain lead projectile and were loaded into production cartridge cases for ballistic testing. The copper projectiles were difficult to crimp into the cartridge cases and the force required to chamber the projectiles was higher than normal. This was due to the increased hardness of copper over lead. The copper projectiles were annealed which reduced the hardness from an average of 72 to 10 on the Rockwell F scale. A groove was cut in the area where the cartridge case is crimped into the projectile to improve the crimp. This reduced the crimping and chambering problem, however, when these projectiles were loaded for maximum ballistic performance and fired, the projectiles did not provide the impulse necessary to function the M16 rifle. The projectiles' average extreme spread for accuracy was 0.37 inches, close to the program's requirement of 0.35 inches. To increase the impulse, 36 grain projectiles (figure 2) were produced and loaded with Winchester (WC663) propellant for maximum ballistic performance in much the same manner as the 32 grain projectiles had been. The fired projectiles were ballistically stable at fifty feet but became unstable at one hundred yards. They, however, provided sufficient impulse to cycle the M16 rifle. To optimize the projectile, the design of the heaviest stable projectile weighing between 32 and 36 grains was initiated. This was accomplished by shortening the 36 grain projectile's heel length in small decrements and firing samples for accuracy. After considerable testing, a 34 grain projectile (figure 3) was determined to best meet the requirements for impulse and ballistic stability. The projectile's diameter was decreased from 0.2240 inches to 0.2220 inches to reduce the friction with the rifle barrel resulting in lower chamber pressures and higher projectile velocities. The accuracy tests conducted with standard production cartridge cases and propellants indicated average extreme spread for this cartridge of about 0.60 inches. A larger sample of the 34 grain projectiles was then fabricated for further evaluations with the concurrently developed non-contaminating primer mixture.

The development of a lead-free primer mixture consisted of choosing the right combination of initiating explosive, oxidizer, and sensitizer. Of the three possible lead-free initiating explosives, diazodinitrophenol (DINOL) was selected. The lead-free, chlorate based, initiating explosive was eliminated due to its corrosive by-products, and the tetrazole based initiating explosive was eliminated due to the lack of sufficient information about its functional capabilities. The partical size of the DINOL required to provide proper rimfire sensitivity measured in the range of 80 to 130 microns. Various combinations of oxidizers and sensitizers were mixed with the DINOL to develop a primer mixture that would function satisfactorily. During the iteration process, (tables 2 and 3), a mixture containing potassium permanganate (a strong oxidizer), mixture 13, prematurely detonated, destroying a remote control mixer. Manganese dioxide (MnO_2) thus was chosen as the oxidizer since it was a relatively strong oxidizer, non-toxic, non-corrosive, and insoluble in water. During the iteration process it was determined two types of mixture sensitizers were required to provide the proper sensitivity. One was the chemical sensitizer, tetrazene, and the other was a physical sensitizer consisting of tiny (about 150 microns) hollow glass spheres.

The primer mixture, loaded in production cartridge cases for design review testing, consisted of 30% DINOL, 30% tetrazene, 20% glass, and 20% manganese dioxide (mixture 16H, table 3). The cartridge cases were primed with various amounts of the new primer mixture, ranging from the volumetric charge used with the standard lead styphnate primer mixture to four times the volume of the lead styphnate primer mixture. The amount of new primer mixture which produced acceptable pressure and velocity relationships was the same volumetric charge as used with the lead styphnate mixture. A thin layer of nitrocellulose foil was added to bond the primer mixture in place and provide additional ignition energy.

With an acceptable primer mixture and projectile design available, a model was devised to evaluate the projectile velocities based on various loads of propellant. This was conducted to determine the functioning range (figure 4) of the M16 rifle. The model indicated a velocity of 1400 feet per second (fps) was required for the prototype projectile to function the M16 rifle. WC371 propellant produced the desired 1400 fps velocity for a 34 grain projectile without exceeding pressure requirements. The propellant was loaded into cartridge cases for tests of the prototype projectile and primer mixture to finalize the prototype cartridge for the design review. The testing conducted during the design review indicated the new cartridge would meet the key performance requirement of eliminating airborne contamination but would not meet the accuracy requirement. The cartridge, however, was close to meeting the accuracy requirement and government approval was granted for production of the prototype cartridge quantity required for the final tests. Minor changes to the propellant, primer, and nitrocellulose quantity were to be made in an attempt to improve the cartridge performance for final testing. The final cartridge configuration was as follows: (see table 4)

Tests Conducted

The cartridge performance results obtained during the testing of the prototype were as follows:

Chamber Pressure. The chamber pressure was tested in a test barrel with sample sizes of one hundred cartridges, temperature conditioned for sixteen hours at the specified temperature (table 5)

The prototype's pressure and velocity variations were higher than desired and they were higher than those experienced during the design review testing. This may have been due to the minor changes made after the design review, increasing the cartridge's performance. The variations were also due to the increased velocity required to provide the impulse to function the M16 rifle with the lighter copper projectile. The Sporting Arms and Ammunition Manufacturers Institute Inc. (SAMMI) recommends a maximum average pressure loading limit of 24,000 psi at ambient temperatures which the prototype ammunition exceeded by 1400 psi. The prototype ammunition exceeded the SAMMI maximum individual pressure of 30,100 at all three temperatures, and the ammunition's pressure standard deviation was about six times that of the control ammunition. Large pressure and velocity variations, however, are frequently encountered in feasibility studies and are typically eliminated during design refinement.

Accuracy Tests. The accuracy tests at 50 feet and 100 meters were conducted simultaneously. (see table 6)

The accuracy goal of an 0.35 inch average extreme spread at fifty feet was not met by the prototype ammunition in the target rifle or the M16 rifle. In fact, the average extreme spread was more than double the goal in a target rifle. The accuracy of both the prototype and control ammunition in the M16 rifle was lower than in the target rifle due to the rimfire conversion kit.

The prototype ammunition's primer mixture and propellant did not reliably ignite in the M16 rifle, resulting in approximately a thirty percent misfire and bullet-in-bore rate. In many of the bullet-in-bore cases, the propellant was not ignited and much of the primer mixture was still intact. The pressure may have vented past the projectile in the conversion kit due to the smaller projectile diameter and the gap where the conversion kit meets the rifling of the M16 rifle. The conversion kit's firing pin strikes a much larger area than the typical rimfire firing pins. This can result in less efficient ignition of the primer mixture and failure to properly ignite the propellant.

The test in a first target rifle was stopped because a cartridge case rim burst in an unsupported area. A second target rifle was substituted and again the test was stopped because of a burst rim in the unsupported area. The burst rims occurred due to high chamber pressures.

Velocity Retention. The velocity retention test consisted of samples of 100 cartridges fired through three velocity screens (see table 7)

The velocity retention test was conducted to determine how quickly the prototype projectiles would lose velocity compared to the lead projectiles (controls). The non-contaminating cartridge was designed for use on fifty foot ranges and at that range the velocity was approximately three hundred feet per second faster than the control ammunition. This was due to the initial velocity increase needed to provide enough impulse in the M16 rifle. The difference in velocity should have no noticeable effect on accuracy at the fifty foot range.

Airborne Contamination. The airborne contamination test was conducted by the U.S. Army Environmental Hygiene Agency. The test consisted of firing prototype and control ammunition in an enclosed volume in an attempt to measure the quantity of contaminates released by both types. The contaminates measured included metals (lead, copper, manganese, and barium) and gases (carbon monoxide, nitrogen dioxide, ammonia, and hydrogen cyanide). A weapon was mounted inside the enclosed volume, with the only opening being a six inch diameter tube from which the projectiles exit (figure 5). A sampling tube was connected to the enclosure and calibrated sampling equipment was used to monitor the atmosphere inside the enclosure. The sampling pumps were started and prototype ammunition was fired at approximately 15 second intervals until five cartridges had been fired in the M16 rifle. The sampling pumps continued to draw the air out of the enclosure until the carbon monoxide monitor indicated that the levels had returned to baseline or stabilized. The test procedure was repeated with control ammunition in the M16 rifle. The rifle used for sampling was changed to a Ruger semiautomatic and the test was repeated, with the prototype and control ammunition. A plot of the gases' concentration levels versus time (figure 6) shows how the gaseous concentration levels caused by the prototype ammunition was higher than the control ammunition. The higher concentrations of nitrogen dioxide and carbon dioxide, in the opinion of the Industrial Hygiene Agency, should not present a health hazard greater than conventional ammunition since the gases are easily diluted and dispersed even in firing ranges with minimal ventilation. Hydrogen cyanide and ammonia were not present in measurable quantitites with either the prototype or conventional ammunition. An analysis of the quantities of metals collected by filtering the pumped air indicated that the prototype ammunition produced far less airborne metallic materials than the control ammunition (table 8). The weight of the copper and manganese contamination produced by the prototype ammunition was about one-thirtieth the weight of the lead and barium produced by the conventional ammunition. In addition, the toxicity of the subsituted materials was much lower than that in the conventional ammunition.

CONCLUSIONS

The testing of the cartridge's performance indicated that the key program goal had been successfully met. The health hazard introduced by the new ammunition was dramatically reduced. The amount of metallic particles collected from the prototype ammunition was only 3% of that produced by the control ammunition. In addition, the toxicity of the prototype's metallic particles was much lower than that of the control ammunition.

The prototype ammunition did, however, exhibit accuracy and pressure variations exceeding those required in the contract and by commercial ammunition specifications. Due to time limitations and the fact that this was only a feasibility study, the optimization of the primer mixture, propellant, and projectile designs were not conducted nor expected. Olin Corporation conducted additional studies and tests on slight variations of the cartridge after the final testing. Favorable results were achieved by making small adjustments to the projectile's diameter to reduce the interference area with the rifle's barrel. The primer mixture still requires further study to determine the most efficient balance of ingredients and particle sizes.

The prototype cartridge is estimated to cost about twice that of the control cartridge. The bulk of the cost increase is due to the higher material cost of the copper projectile.

RECOMMENDATIONS

It is recommended that the progress made by this program be brought to completion through a follow-on program. When finalized, this lead-free ammunition will allow the resumption of training in many of the closed indoor firing ranges without installing additional ventilation systems.

Table 1. Test matrix

Test	Test barrel P	Test barrel C	M16 rifle P	M16 rifle C	Commercial rifle P	Commercial rifle C
	Number of rounds to be fired					
1. Chamber pressure	100	50	NA		NA	
2. Accuracy (50 ft)	100	50	100	50	100	50
3. Accuracy (300 ft)	100	50	100	50	100	50
4. Velocity (15 ft)	50	25	50	25	50	25
5. Velocity (50 ft)	100	50	100	50	100	50
6. Velocity (300 ft)	100	50	100	50	100	50
7. Airborne contamination	NA		20	20	20	20

P = Prototype ammunition C = Control ammunition

Table 2

Caliber .22 lead-free primer mix evaluation

Ingredient/mix no.	1	2	3	4	5	6	7	8	9	10	11	12	13	14	15	15A	15B	15C	15D	15E
DINOL	35[1]	45[1]	30[1]	45[2]	45[1]	35[1]	30[1]	45[2]	45[1]	40[2]	45[2]	15[2]	45[2]	45[2]	40[2]	35.5[2]	43.6[2]	31.1[2]	35.5[2]	35.5[2]
Tetrazene	5	3	3	3	3	13	5	3	3	40	5		3	3	30	26.7	32.7	23.3	26.7	26.7
Glass	22	10	10	10	10	10	22		10	10		22	10	10	10	20		30	10	10
Nitrocellulose	25	5												5[4]						
Barium nitrate	6	37	37	37		37	38	37			37	28		37						
Petn			5	5	5	5	5	5	5		5	5	5							
Lead styphnate, normal			15									30								
Aluminum	7																			
Sodium nitrate					37															
Q-Cell glass								10									1.9			
Potassium chlorate									37	10									10	
Antimony sulfide											8									
Potassium permanganate													37							
Hexanitromannitol															20	17.8	21.8	15.6	17.8	17.8
Manganese dioxide																				10
Percent Fired																				
In 22LR case																				
Single charge	0	0	20	0	0	0	0	4	4	-	-	-	*	-						
Double charge										48	4	76		4						
Triple charge										96	4	68		64	0	0	0	0	0	0
In loaded round																				
Single charge		10	80	0	10	30	2.5	4	-		-	-								
Double charge										85				40						
Triple charge										95				45	0					

1 - Hercules batch 006
2 - Hercules batch 136
3 - Olin R & D
4 - Ball milled

* Mix detonated in mixer

Table 3

Lead-free prototype mix no. 10 variations

Percent ingredients/mix No.	16	16B	16C	16D	16E	16F	16G	16H
DINOL (Olin)	40	30	35	30	30	30	25	30
Tetrazene	40	30	35	30	30	30	25	30
Hexanitromannitol								
Potassium chlorate	10		15	20				
Manganese dioxide		20			20	20[1]	25	20[2]
Glass	10	20	15	20	20	20	25	20
Percent fired								
In .22 long rifle case (2 oz. ball)								
Single charge							12	8[3]
Double charge				64	94	24	98	76[3]
Triple charge	64			100	100	100		
Quadruple charge		68	68	96	100			
Heavy								20
1.5 charge								16
In loaded round	See ballistic tables							

1 - Ball-milled, passed 140 U.S. sieve
2 - 88 to 177 micron cut
3 - All misfires showed partial ignitions without propagation

Table 4. Final cartridge configuration

Primer mixture composition (16H)	30% R&D DINOL 30% Tetrazene 20% Manganese dioxide (88 to 177 micron) 20% Glass (140 micron)
Bullet	34 gr. Copper
Case	Standard caliber .22
Primer charge weight	0.27 gr. avg. 0.32 Max. 0.22 Min. 0.028 Standard Deviation (SD)
Propellant	WC371 SM11 @ 2.9 gr.
Bullet pull	35 lb. min. avg.
Loaded length	0.980 + 0.005 in.
Lubricant	Standard rimfire lubricant

Table 5. Chamber pressure (psi/100)

Temperature (°F)	Average Prot	Average Cont	Maximum Ind Prot	Maximum Ind Cont	Minimum Ind Prot	Minimum Ind Cont	Standard Deviation Prot	Standard Deviation Cont
70	254	221	386	244	104	198	54	9
140	221	235	327	253	111	205	53	9
-40	224	215	364	242	81	197	65	9

Table 6. Accuracy tests

Ammo	Gun	50 feet	100 meters	Notes 1
Cont	Note no. 6	0.35	2.15	2
Prot	Note no. 6	0.73	4.62	3
Prot	Note no. 7	0.91	5.27	4
Cont	Note no. 8	0.87	4.97	2
Prot	Note no. 8	3.58	25.73	5

Notes:

1. The accuracy test was conducted at 100 meters instead of 100 yards as in table 1.
2. Sample size was ten targets of ten rounds each.
3. Sample size was seven targets of ten rounds each, stopped test due to blown cartridge head and possible gun damage.
4. Sample size was four targets of ten rounds each, stopped test due to blown cartridge head and possible gun damage.
5. Sample size was two targets of ten rounds each, stopped test due to misfire or bullet in weapon bore rate of 30%.
6. Winchester model M52D match .22 long rifle.
7. Winchester model M52D match .22 long rifle replaced previous rifle.
8. M16 rifle with M261 rimfire conversion kit.

Table 7. Velocity retention test

Ammo	Gun	Screen 1 15 Feet vel	sd	Screen 2 50 Feet vel	sd	Screen 3 100 Feet vel	sd	Notes
Prot	Test Barrel	1438	69	1383	65	1004	36	1
Cont	Test Barrrel	1117	6	1097	15	946	7	
Prot	M52D	1455	72	1402	68	1028	43	1,2
Cont	M52D	1114	5	1089	13	943	5	
Prot	M16	1229	98	1194	91	960	46	1
Cont	M16	1106	5	1080	8	923	9	

Notes:

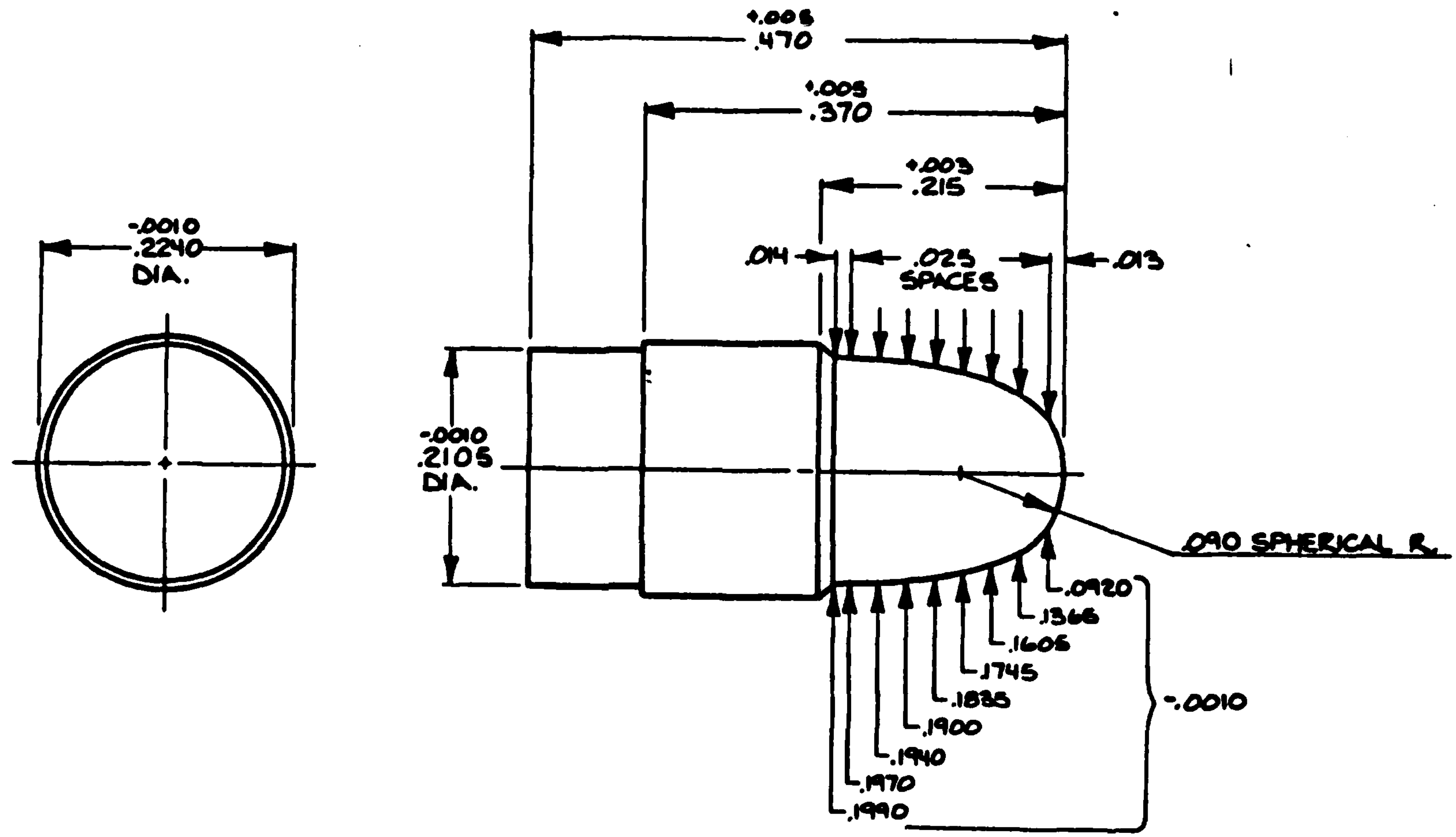
1. The test results do not include prototype projectiles which did not trigger all three velocity screens.
2. The sample size was 58 cartridges; test stopped because of blown cartridge case head.

Table 8. Metals analysis results

Ammo*	Sample No.	Lead	Copper	Barium	Manganese
		Total milligrams during 65 minutes 5 Rounds per sample			
Pb-Ruger	1-24	1100.19		83.56	
	2-24	3091.01		283.38	
Pb-M-16	4-22	2637.59		210.22	
	5-23	4259.71		293.85	
Cu-Ruger	6-23		19.09		19.88
	7-23		54.73		52.37
Cu-M-16	2-22		72.37		26.49
	3-22		119.56		43.105
Pb-Ruger	Avg (2)	2095.6		188.47	
PB-M-16	Avg (2)	3448.65		252.035	
Cu-Ruger	Avg (2)		36.91		36.125
Cu-M-16	Avg (2)		95.965		34.7975
Lead	Avg (4)	2772.125		94.235	
Copper	Avg (4)		56.4375		35.46125

* Pb-Ruger means conventional (lead) ammunition fired from a Ruger rifle.
Pb-M-16 means conventional (lead) ammunition fired from an M-16 rifle.
Cu-Ruger means prototype (copper) ammunition fired from a Ruger rifle.
Cu-M-16 means prototype (copper) ammunition fired from an M-16 rifle.

Avg (2) means the average of the two samples.
Avg (4) means the average of the four samples.



NOTES:

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Figure 1. Bullet, 32 grain, copper .22 long rifle, lead-free

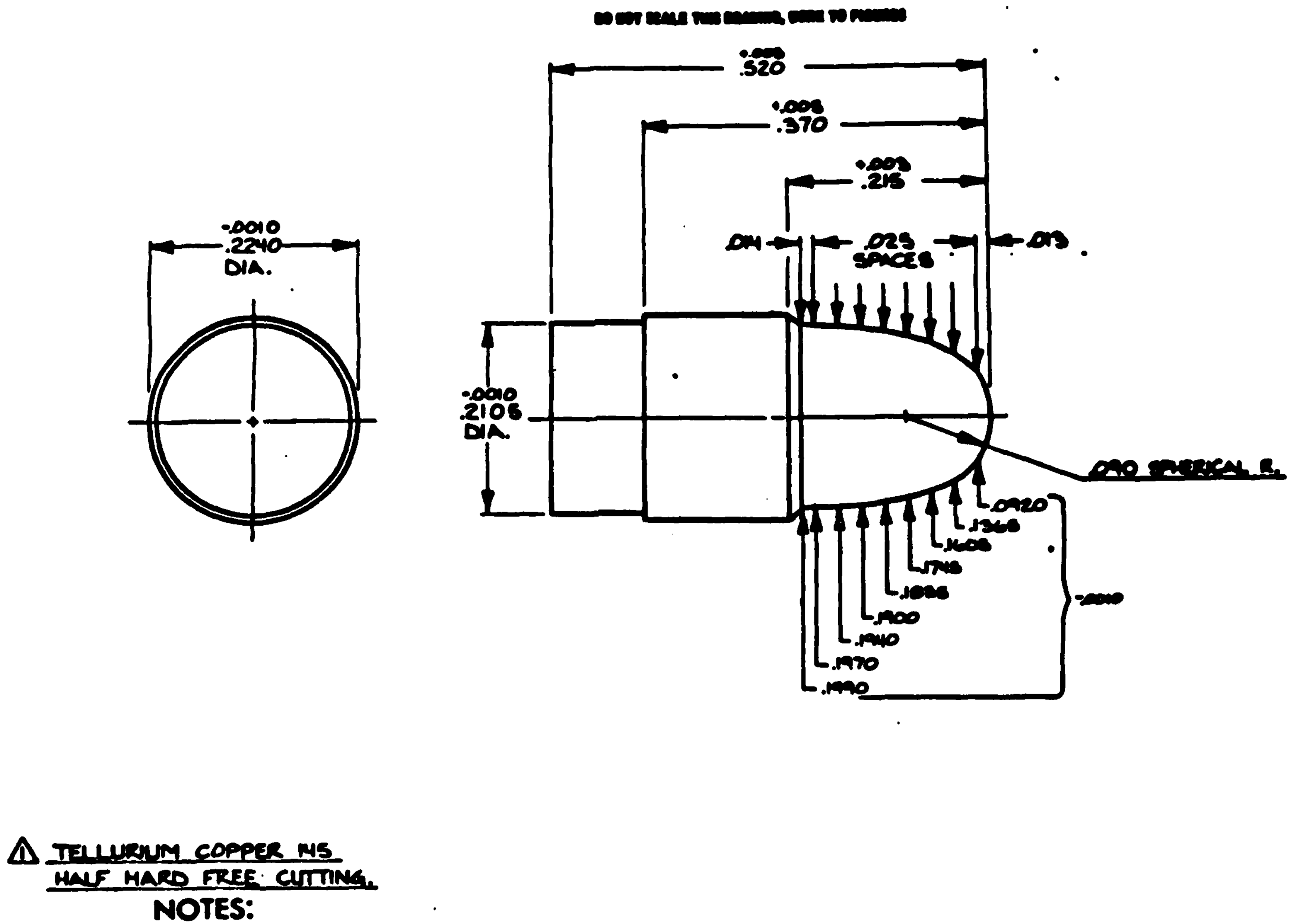


Figure 2. Bullet, 36 grain copper, .22 long rifle, lead-free

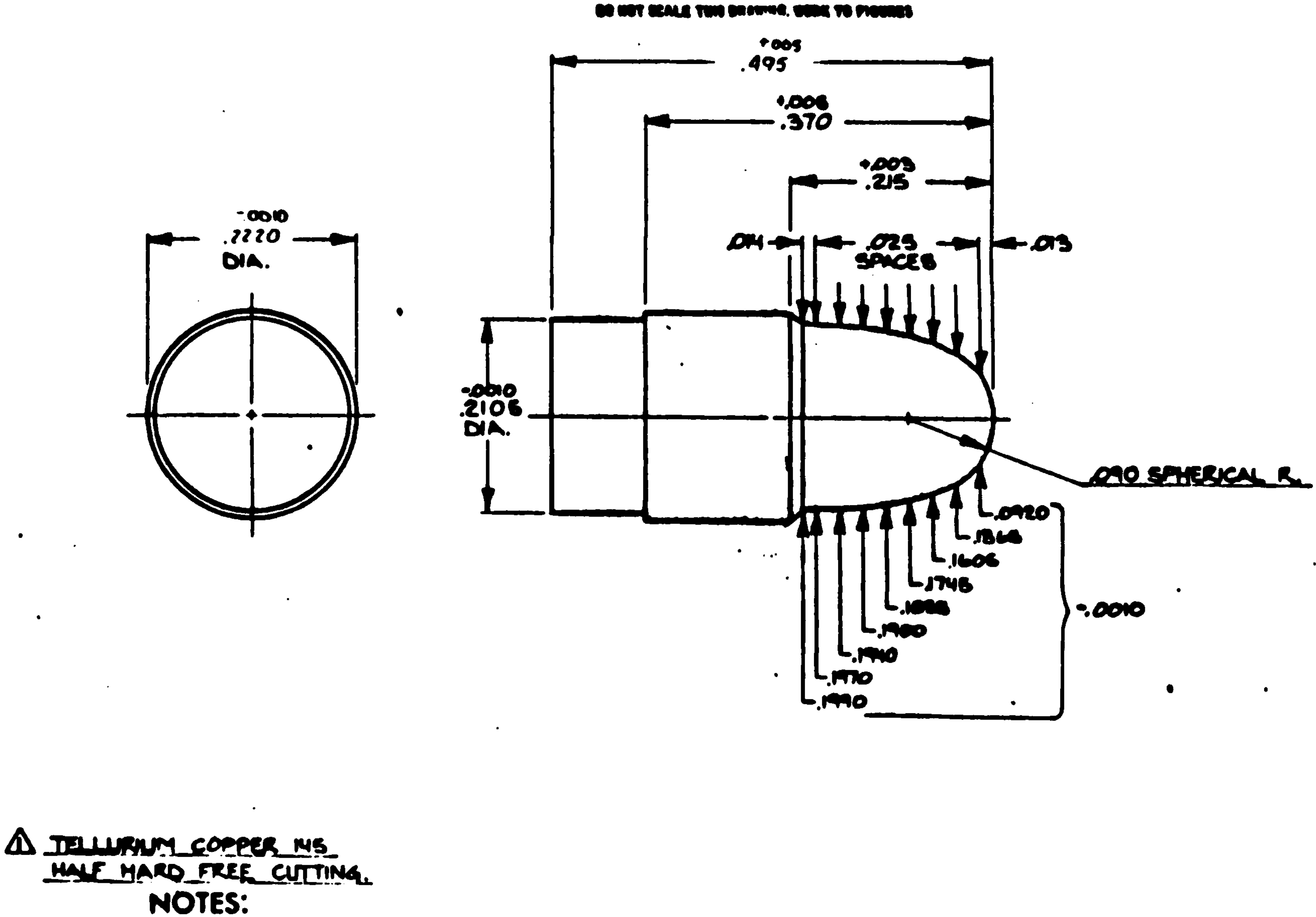


Figure 3. Bullet 34 grain copper, .22 long rifle, lead-free

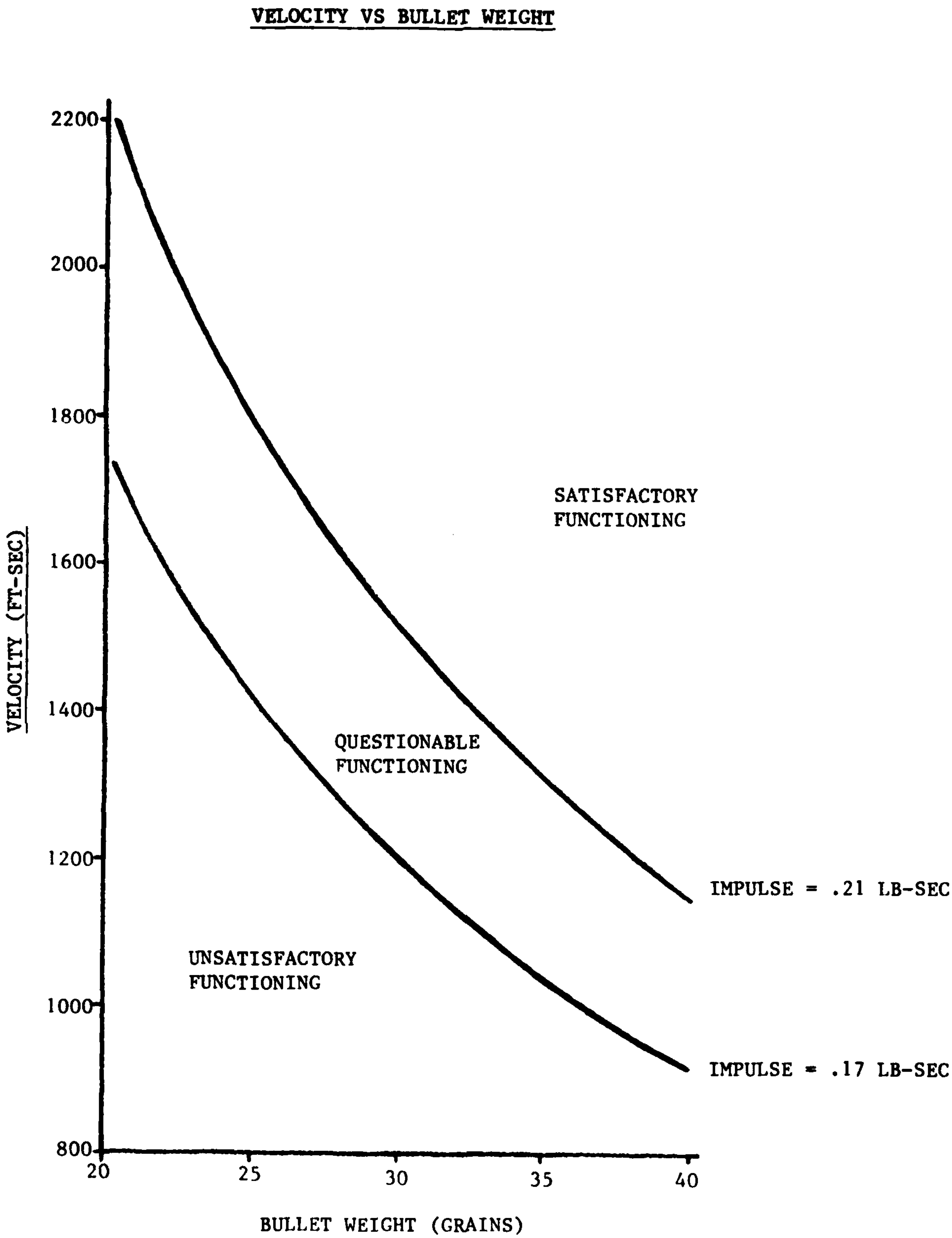


Figure 4. Proper functioning - impulse ranges

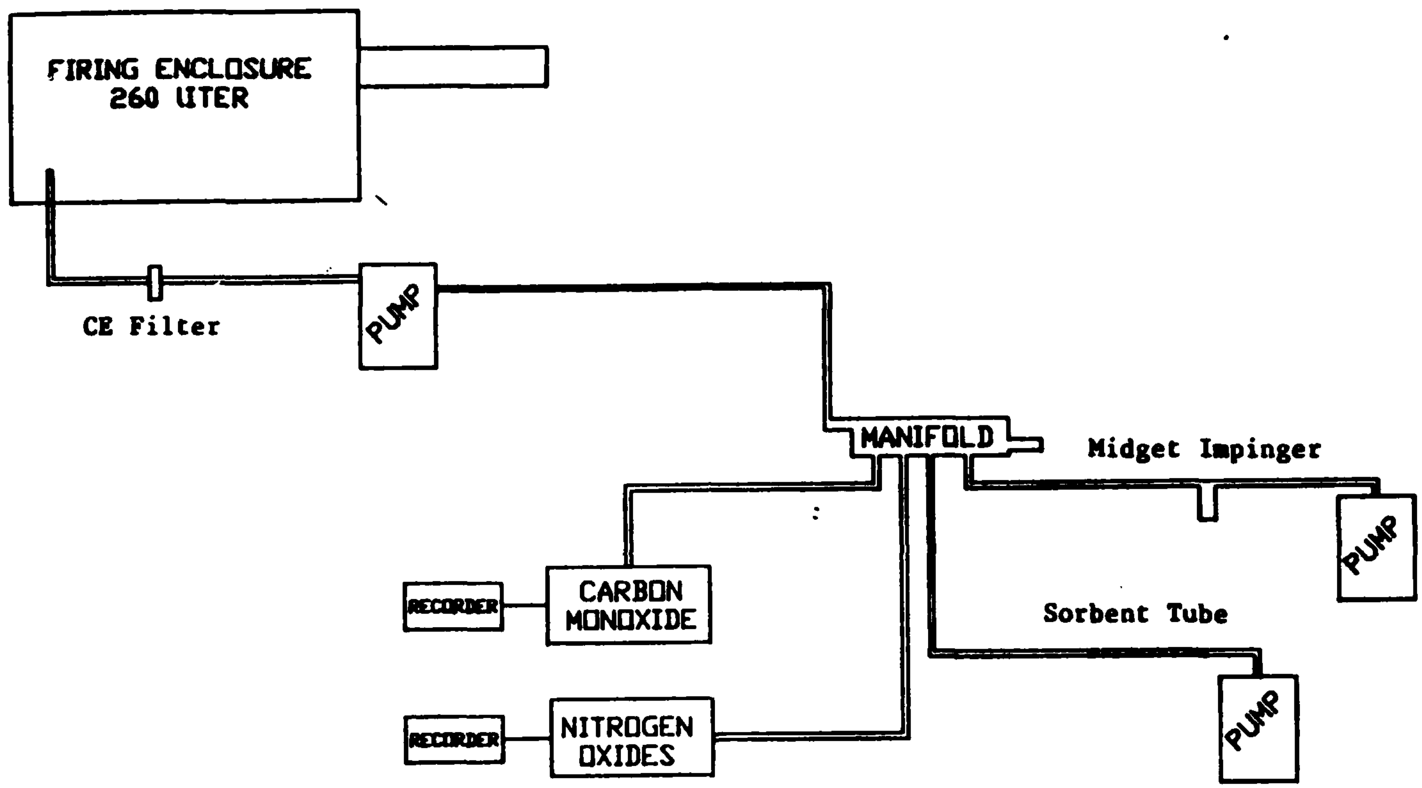
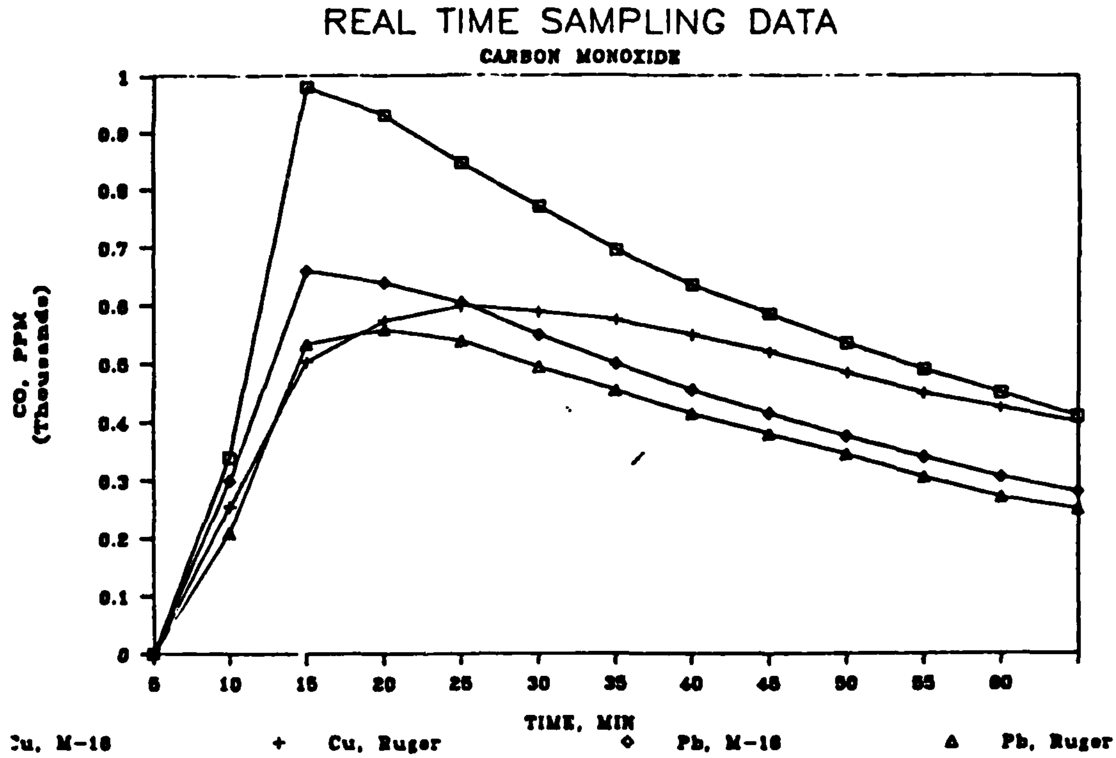


Figure 5. Airborne contamination test



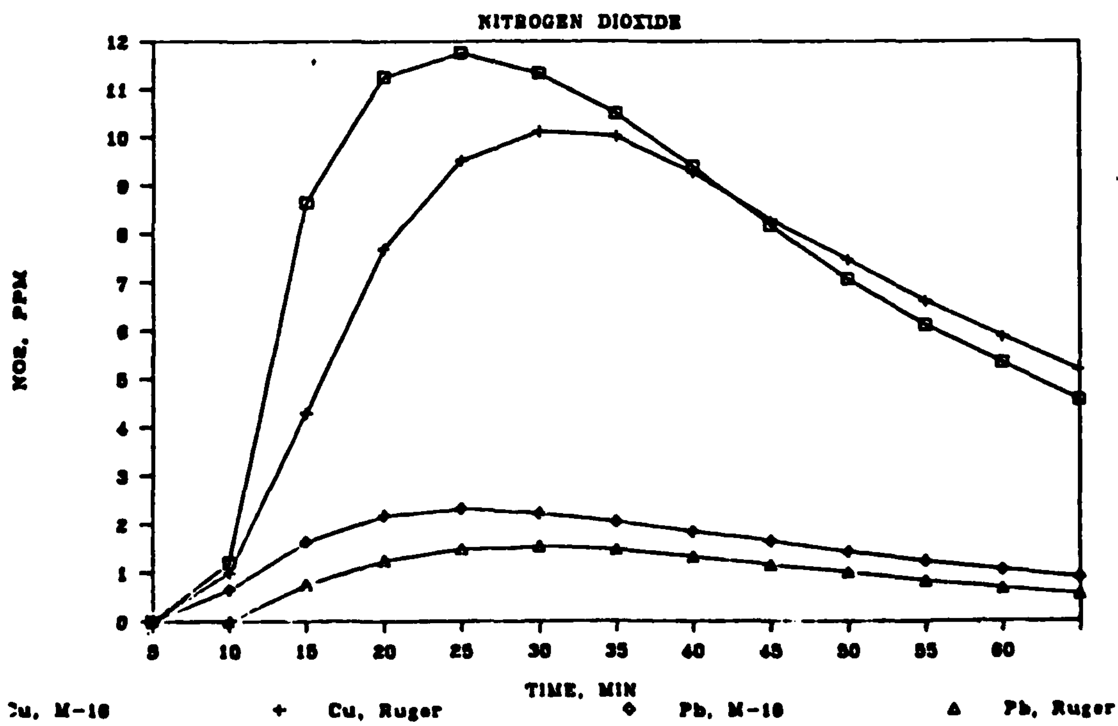


Figure 6. Gas concentration levels

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